STATE OF CALIFORNIA

AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

AUDIT PROCEDURES FOR AIR QUALITY MONITORING

APPENDIX AD

PERFORMANCE AUDIT PROCEDURES FOR THROUGH-THE-PROBE CARBONYL AUDITS

MONITORING AND LABORATORY DIVISION

MAY 2002

APPENDIX AD

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VOLUME V

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APPENDIX AD.1

PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE CARBONYL AUDITS

MONITORING AND LABORATORY DIVISION

MAY 2002

AD.1 THROUGH-THE-PROBE CARBONYL AUDIT PROCEDURES

AD.1.0 INTRODUCTION

AD.1.0.1 GENERAL INFORMATION

Carbonyl through-the-probe (TTP) audits are conducted annually at each site by the Quality Assurance Section (QAS) staff. A sample of audit gas with known (assigned) concentrations is collected on a carbonyl cartridge for a three-hour period and then analyzed by the laboratory. The sample is run, wherever possible, in conditions duplicating a routine ambient run. The analytical laboratory results are compared with the known concentrations, and a percent difference calculated.

The purpose of a TTP audit is to assess the accuracy of the total measurement system, including errors inherent in contamination in transport, effects of sample pump and probe, and laboratory error.

AD.1.0.2 FIELD NOTIFICATION

The QAS arranges the audit with the station operator 10 days to 2 weeks prior to the audit date. The station operator is requested not to notify the laboratory that the cartridge is an audit cartridge. No special or differentiating markings are put on the cartridge or holding container.

AD.1.0.3 CAUTIONS

In order to obtain accurate data, it is necessary to avoid contamination. Whenever possible, silica-lined stainless steel tubing will be used to introduce the audit sample to the probe inlet. All lines and fittings in the dilution unit must be cleaned periodically and capped when not in use. Also, during each audit there must be a positive pressure at the manifold “T” (1 liter/per minute minimum excess bypass flow) where the dilution system output connects to the sample probe.

AD.1.1 AUDIT PROCEDURES

AD.1.1.1 APPARATUS

1. Dilution Unit
2. Pure Air Generator
3. ¼" teflon tubing
4. Tygon® tubing
5. Container for Drain
6. Audit Cylinder
7. Stainless Steel Regulator
8. Barometric Pressure Gauge
9. Thermometer
10. Ziploc® Bag

AD.1.1.2 DETERMINATION OF DILUTION RATION

The dilution ratio to be used for the audit is defined as follows:

$$\text{Dilution Ratio} = \frac{\text{Gas Flow}}{\text{Air Flow + Gas Flow}}$$

The dilution ratio chosen for an audit is dependent upon several factors, including assigned cylinder concentrations, required minimum air flow, gas flow (cannot exceed 1000 cubic centimeters per minute (CCPM)), and the requirement to generate concentrations greater than the minimum detectable limit. The concentration in the audit gas stream, in general, is in the range of 1.0 to 15.0 ppb.

1. Desired gas concentration (assigned value): 9.0 ppb

   Assigned NIST Cylinder Value: 900 ppb

   $$\text{Dilution Ratio Calculated} = \frac{9.0 \text{ ppb}}{900.0 \text{ ppb}} = .01$$

2. Find the probe flow and add the required manifold bypass flow of 1.0 LPM. For example, assume the probe flow is equivalent to 3.5 LPM.

   Required Air Flow = 3.5 LPM + 1.0 LPM
   = 4.5 LPM (True Flow)

   = 4500 CCPM

3. Substitute and Solve for Gas Flow

$$\text{Dilution Ratio} = \frac{\text{Gas Flow}}{\text{Air Flow + Gas Flow}}$$

$$.01 = \frac{\text{Gas Flow}}{\text{4.5 LPM + Gas Flow}}$$

Gas Flow = 0.0455 LPM
= 45.5 CCPM (True Flow)

4. Using the dilution system correction equations from the lab's latest calibration report (certified biannually), calculate the required air and gas flow rates for the Dilution Unit. The key pad on the dilution unit will be used to set the flow rates for the desired mass flow controllers. The following results are from a typical calibration:

Air: Display = True Flow (.0011) - .0435

4500 (.0011) - .0435 = 4.9065 LPM
= 4907 CCPM

Gas: Display = True Flow (1.0933) + .5284
45.5 (1.0933) + .5284 = 50.3 CCPM

AD.1.1.3 AUDIT DATA REPORTING

Final verified audit data should be submitted to the operating agency as soon as possible. Delays may result in data loss; a sampler out of audit limits is also out of calibration limits, and the data collected may be invalid. If a sampler exhibits unsatisfactory agreement with the verified audit results (audit differences in excess $\pm$20%), a calibration should be performed before the next run day and an Air Quality Data Action (AQDA) request should be initiated.

AD.1.1.4 PERFORMANCE AUDIT FREQUENCY

For Photochemical Assessment Monitoring Stations (PAMS), conduct a TTP audit of each sampler per monitoring network during the PAMS season (July through October). Each sampler will be audited at least once per year.

AD.1.1.5 LEAK CHECK PROCEDURES

During the FIRST leak test, all solenoid valves upstream and downstream of the cartridges are checked. First, a zero check is initiated for channels A, B, and C. The zero check checks for leaks in the mass flow controllers. During the zero

check, the voltage offsets are determined and subtracted from the channel readings for the remaining leak check sequences. The leak test and performance audit should be performed with the cartridges in place. A leak test is initiated using the following procedure.

1. Install a carbonyl cartridge into either channel A, B, or C by disconnecting the cartridge sampling lines (turn and pull down) and unscrewing the cartridge holders. (See Figure AD.1.1.1). Prior to installing the cartridge, remove the plastic caps located at each end of the cartridge. Do not discard the caps. Additionally, verify that the o-ring inside the cartridge holder is in place.

   NOTE: Use gloves when handling the cartridge.

2. Press **EXIT** twice to return to the main screen #1 (Default Screen). It should read "Idle".

3. Move to the main screen #7 (Leak Check Screen) by pressing the **RIGHT ARROW** 6 times.

4. Press **SELECT**. The Unit # will be underlined.

5. Press **SELECT**. The Unit 1 underline blinks. If you need to change the unit number, use the arrow keys. When desired unit is displayed press **EXIT**.

6. Exit will prompt "Begin Check? - N".

8. Press **SELECT**. "N" will blink. Press **RIGHT ARROW** to display "Y".

9. Press **EXIT**. Leak check will initiate. The leak check will cycle through all positions. The value for the flow rate of the tube (position) being audited should be close to zero.

   NOTE: Leak check will run automatically. During the leak check, if a leak is evident, trouble shooting can be performed to repair the leak. In the event the instrument does not pass the leak check test, replace the existing cartridge with a new one. The cartridge may be bad. Run the leak check again. If a leak persists, you may try another holder, or report the failure to the station operator and determine if the problem can be repaired.

10. Once the position (tube) being audited has been leak checked and the value is close to zero, you may abort the leak check. Press the **LEFT ARROW** to prompt the Abort Leak Check screen. Press **SELECT** then **RIGHT ARROW** to change the "N" to a "Y". Press **EXIT**. The leak check will abort.

The SECOND leak check will test the entire system including the probe line. With the cartridge in place, cap the sampler probe inlet at the roof with a stainless steel fitting, then follow the procedures under Section AD.1.1.7 to manually turn the sampler on. Once the sampler is running, verify that the flow reads close to zero or the same as in the first leak check. Uncap the probe and continue with the audit.

If the flow is not close to zero or does not read the same as in the first leak check, check all fittings, notify the site operator, and determine if the leak is repairable. If leak persists, do not continue with the audit. Issue an Air Quality Data Action request.

Prior to conducting the TTP audit, print a copy of the instrument's status (if the unit has printer capabilities). From the main screen #1 (Default Screen), press **SELECT**. Press **RIGHT ARROW** until "Print Full Report" is displayed. Press **SELECT** and **RIGHT ARROW** to change to "Y". Press **EXIT**. The report will print. The print-out will provide the auditor with a record of the instrument's settings. Once the report has printed, press **EXIT** again.

AD.1.1.6 STATION PREPARATION

(See Figure AD.1.1.2 for a diagram of the Audit Set-up)

1. Connect ¼" teflon tubing, approximately 50 feet long, to the probe inlet using a "T" fitting. One end of the "T" will be open to ambient air to prevent pressurization of the sampling system. The other end of the teflon tubing is connected to the output port of the dilution unit inside the air monitoring station.

   NOTE: Connect a Vol-O-Flow to the open end of the "T" configuration to verify a positive flow to avoid pressurization of the sampling system.

2. Set up the portable Dilution Unit and Pure Air Generator inside the station. Pure Air should go to Port 1 by means of teflon tubing. Teflon tubing should be attached to the vent port on the Pure Air Generator and.

directed outside of the station building. Also, attach tygon® tubing to the drain port on the Pure Air Generator and collect expelled water in a suitable container.

NOTE: Humidification is not required for TTP carbonyl audits.

CAUTION: If using the old configuration of the Pure Air Generator (no flow restriction on output), do not turn on generator unless it is connected to the Dilution Unit. Water damage and contamination will occurr in the Pure Air Generator.

3. Turn on the Dilution Unit and Pure Air Generator. Start a half-hour purge of the whole sampling system

4. Install the stainless steel (SS) regulator on the audit cylinder and flush three times. To flush the regulator, open the cylinder and pressurize the regulator. Close the cylinder and bleed of pressure through the regulator valve. Repeat this two more times, then connect the regulator to the dilution unit (Port #3) using ¼" SS tubing.

5. Set the gas and air flows on the Dilution Unit to get the desired dilution ratio of .01 (See Section AD.1.1.2) while providing enough air to get at least 1 LPM excess flow at the manifold "T". To have a valid audit, the system must have positive pressure at the manifold "T" to ensure the audit sample is not contaminated by ambient air. Check the audit cylinder regulator to ensure there is an output of at least 25 psig.

   NOTE: Knowing the sampler flow demand, the following relationship is used to estimate the minimum required air flow:

   Required Air Flow = Sampler Flow Demand + 1 LPM Bypass Flow

6. After the half-hour zero air purge, open the valve on the gas cylinder and adjust the output pressure to 25 PSIG. **Allow 30 minutes of diluted gas to purge the entire system.** Record the target air and gas flow rates on the TTP Carbonyl Sampler Audit Worksheet (Figure AD.1.1.3).

7. Record the station temperature and barometric pressure on the worksheet. This will be the initial temperature. The temperature and barometric pressure will be taken again at the end of the three-hour sampling period and an average calculated.

AD.1.1.7 THROUGH-THE-PROBE AUDIT PROCEDURES

1. From the main screen #1 (Default Screen) on the sampler, move to main screen #7 (Leak Check Screen) by using the **RIGHT ARROW** six times.

2. Press **SELECT** followed by the **LEFT ARROW**.
   The screen will display the following:

   Manual Run Unit 1
   CH-A Start? N

3. Press **SELECT**. Unit # will blink. Enter the desired unit # using the arrow keys. If unit one is being used, simply use the **RIGHT ARROW** to move you to CH-A.

4. Once CH-A is underlined press **SELECT**. CH-A will blink to indicate a change can be made. Use the arrow key to change to the channel being audited. When the correct channel or position is displayed, press **EXIT**.

   NOTE: If you are auditing Channel C, the display will read T1-8. For example, if you are auditing Channel C, Tube 2, the display will read T2.

5. Press **SELECT** followed by the **RIGHT ARROW** to change the "N" to a "Y". Press **EXIT**. The sampler will begin to run.

6. Return to the main menu (press EXIT twice). Press **RIGHT ARROW** once. This screen (Main Screen #2) displays the flow rate of the channels. Record this value on the worksheet under sampler flow rate. This flow rate is necessary for determining the volume of air collected on the cartridge.

7. Check Dilution Unit and record target and actual air and gas flow rates.

8. Record Start Time. Also, verify that the temperature and barometric readings have been taken and recorded on the worksheet.

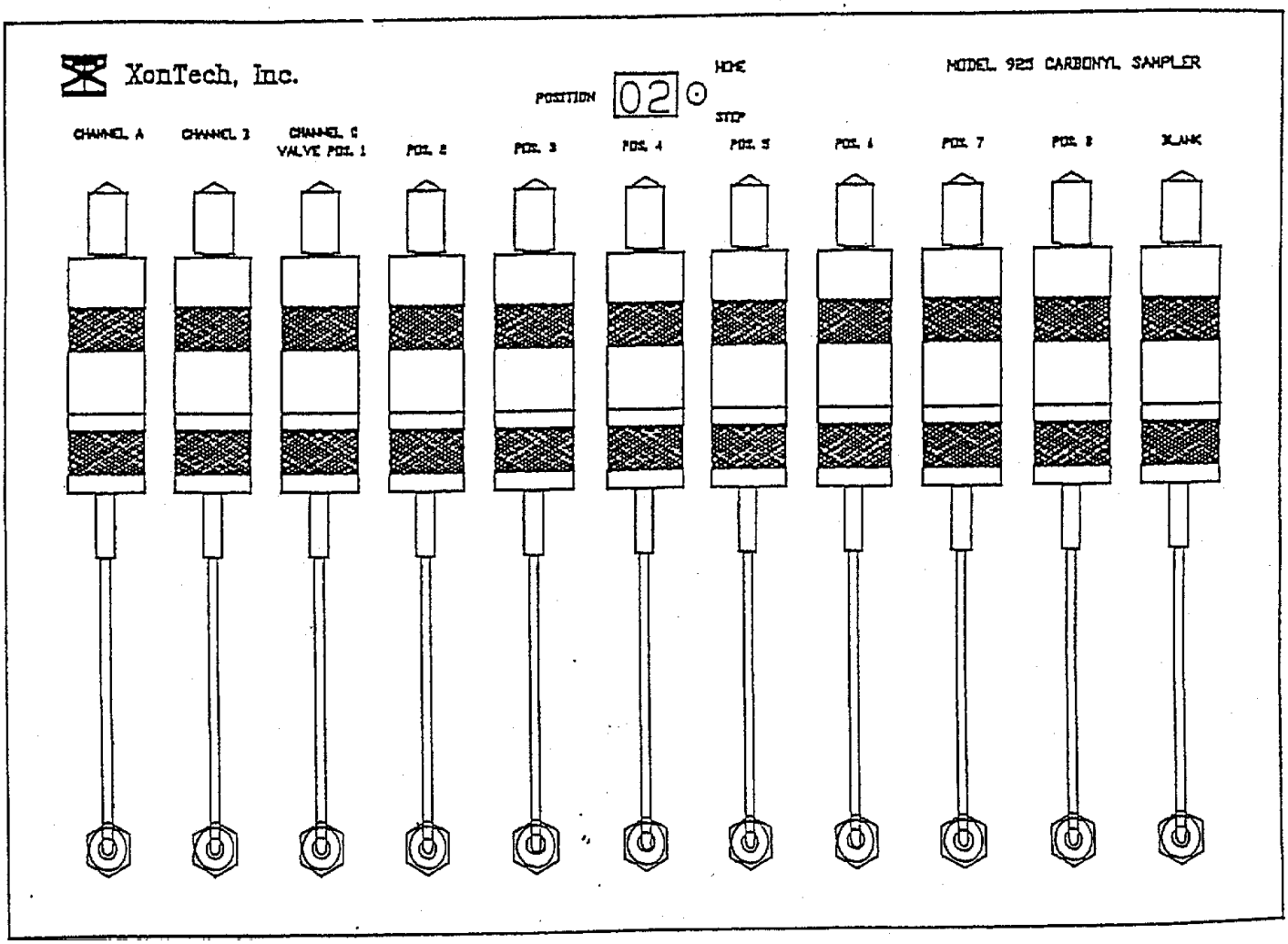

Figure AD.1.1.1
Sampler Diagram

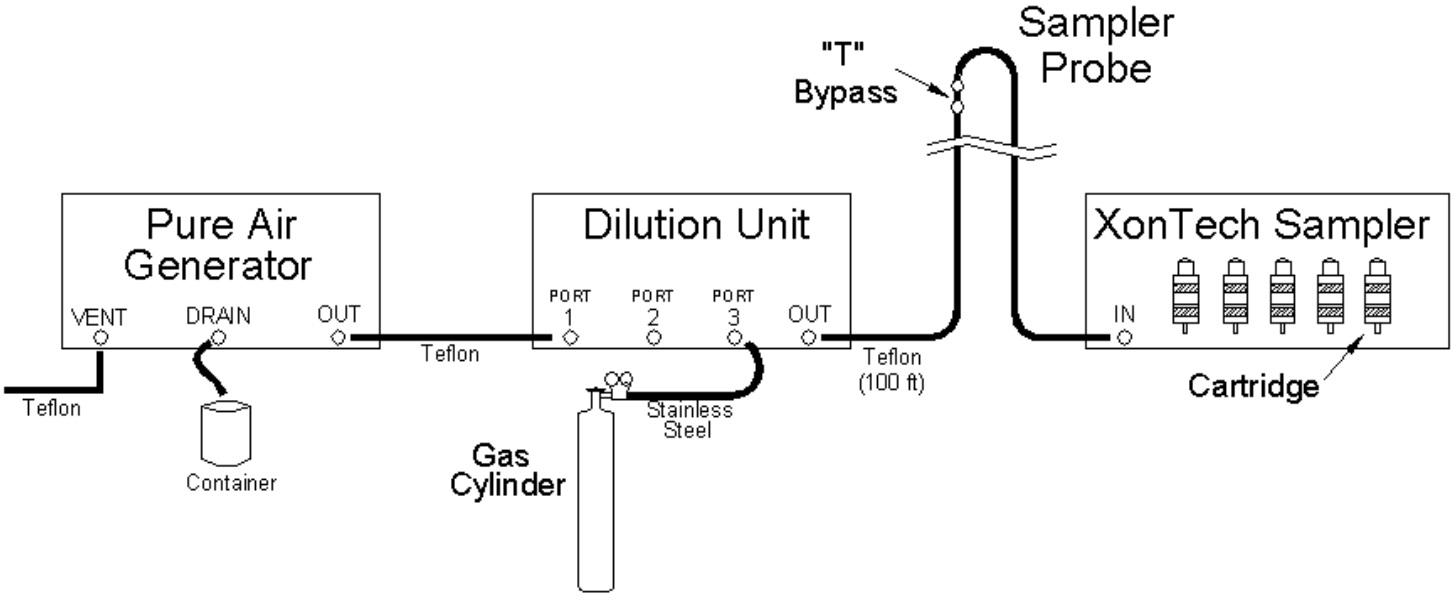

Figure AD.1.1.2
Diagram of Audit Setup

QA AUDIT WORKSHEET
XONTECH 925 CARBONYL SAMPLER

Site Name: _____ Site Number _____ Date: _____

Address: _____ Agency: _____

Technician: _____ Auditors: _____

Quarter: 1[ ] 2[ ] 3[ ] 4[ ] Standards Version: _____ Year: _____

Sampler Information

Make and Model: _____ Channel Audited: _____

Serial/ID#: _____ Tube # Audited: _____

Cal. Date: _____

Cal. Equipment Cert. Date: _____ Sampler Flow Rate: _____

Flow Audit Information

Audit Point	Sampler Flow	Audit MFM Response
Channel A		
Channel B		
Channel C		

Barometer Information	
ID#:	
Initial Reading	Final Reading

Carbonyl Audit Information

Dilution Unit Information
Make/Model:
ID#:
Cal. Date:

Pure Air Unit Information
Make:
Model:
ID#:

Purge and Sample Times	Start	Stop
Zero Air Purge (2 hours)		
Audit Gas Purge (30 minutes)		
Audit Gas Sample Period (3 hours)		

Audit Cylinder Information		
ID#:		
	Initial	Final
Gauge Pressure		

Environics Target Flows	
Port #1	ccm
Port #3	ccm

Environics Actual Flows	
Port #1	ccm
Port #3	ccm

COMMENTS: _____

Air Resources Board
Quality Assurance Section

QA X925-1
Revised 03/02

Figure AD.1.1.3
TTP Carbonyl Sampler Audit Worksheet

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MONITORING AND LABORATORY DIVISION

FEBRUARY 2000

AD.2.0 POST AUDIT CONFIGURATION

1. After the sample duration, verify the flow values and note any deviations on the worksheet. Return to the leak check screen by using the **RIGHT ARROW** key. Press **SELECT**.

2. Screen display will read the following:

   Manual Run Unit 1
   CH-A Stop? N

   The "N" will be underlined. Press **SELECT**. The "N" will begin to blink. Use the arrow keys to change "N" to "Y". Press **EXIT**. The unit will shut down.

3. Press **EXIT** twice to return to main screen #1. Record End Time on the worksheet. Record station temperature and barometric pressure on the worksheet. This will be your final temperature and barometric pressure.

4. Close the main valve on the audit cylinder and purge the regulator by bleeding off the remaining gas through the regulator valve. Remove the SS regulator.

5. Use gloves to remove the audit cartridge from the sampler. Replace the plastic caps on the ends of the cartridge. Place cartridge in Ziploc® bag. Mark the bag either with tape or a piece of paper placed inside bag, and identify date and site number.

   NOTE: The cartridge needs to be placed on ice or in a refrigerator within 24 hours of sampling.

6. Run a five-minute clean air purge. When complete, disconnect the sample probe line.

7. Switch off the sampler, the Pure Air Generator and the Dilution Unit.

8. Disassemble all audit lines and cap each to prevent contamination.

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PERFORMANCE AUDIT PROCEDURES FOR THROUGH-THE-PROBE CARBONYL AUDITS

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FEBRUARY 2000

AD.3.0 POST AUDIT CALCULATIONS

AD.3.1 CORRECTION FOR AMBIENT CONDITIONS

The Environics display readings for the air and gas are to be adjusted to compensate for ambient conditions. Apply the following equation to both the air and gas flow display readings. This will then be the actual flow rates need to determine the dilution ratio. You must first apply the slope and intercept to calculate the actual flow.

Actual Flow = (Display Reading) * (Slope) $\pm$ (Intercept)

$$\text{Standard Flow} = \text{Actual Flow} \frac{(273.15 + \text{Temp °C.})}{298.15} \frac{(760 \text{ mmHg})}{\text{B.P.}}$$

Where B.P. = Barometric Pressure, mm Hg
Temp. = Ambient Temperature in °C

AD.3.2 VOLUME OF AIR COLLECTED

The following equation is to be used to determine the volume of air collected during the audit.

(Sampler Flow) * (60 min/hour) * (Duration in hours) = Liters of Air Collected

AD.3.3 SAMPLE COLLECTED IN PPBV

Upon completion of analysis, the laboratory will send you a copy of the results indicating the amount of sample in micrograms for each compound detected. The following equation is to be used to determine the amount of each compound in parts per billion by volume.

$$\text{ppbv} = \frac{(24.478 \times 10^{9}) \times G}{MW \times V}$$

Where
G = grams of carbonyl
V = volume of air collected in Liters
MW = molecular weight of carbonyl (grams/mole);

Formaldehyde = 30.0162
Acetaldehyde = 44.0530
Acetone = 58.1

AD.3.4 CALCULATION FO PERCENT DIFFERENCE

Calculate the percent difference for acetaldehyde using the following equations:

Assigned Value = Dilution Ration x Assigned Cylinder Value.

$$\text{Percent Difference} = \frac{(\text{Measured Concentration} - \text{Assigned Cylinder Value})}{\text{Assigned Cylinder Value}} \times 100$$

The results are presented in a report as shown in Figure AD.3.4.1.

Quality Assurance Carbonyl Laboratory Audit Report

Station/Van Audit Data & Results

Station Data Indicated Conc. (PPB)	Van Data Actual Conc. (PPB)	Percent Difference
6.9	8.3	*-16.9%*

Audit Calculations

Actual Conc. = Dilution Ratio*Audit Cylinder Acetaldehyde Concentration

Corrected Flow = (Display)*(Temp in Kelvin/298.15)*(760/Barometric Pressure)

Dilution Ratio = (Corrected Gas Flow)/(Corrected Gas Flow+Corrected Air Flow)

Port	Display (ml)	Corrected (ml)		
Air Flow	1297.0	1302.3	Barometric Pressure in mmhg	753
Gas Flow	10.867	10.912	Temperature in Kelvin	296.65
			Audit Cylinder Acetaldehyde Concentration in PPM	0.994

Indicated Conc. = (24.478* Reported Weight*1000)/(44.053*Total Volume)

Total Volume = (Corrected Gas Flow+Corrected Air Flow)*Minutes/1000

Reported Weight in ug	2.922
Audit Duration in Minutes	179

Instrument/AIRS Information

ARB Number	34295	AIRS Number	060670006
Audit Date	12/31/99	Instrument Manf.	XONTECH
Version	0	Model	925
Quarter	4	Serial Number	1234
Van	B	Last Calibration	11/30/99

General Comments

Figure AD.3.4.1
Sample Audit Report